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Magnetic Properties of FePt Nanoparticles Annealed With NaCl

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FePt nanoparticles have the potential to extend the data density of magnetic recording beyond 1 Tbit/in². The phase transformation from low anisotropy, face-centered cubic to face-centered tetragonal with high anisotropy is essential and complex. The samples measured in this paper were annealed in a mixture with fine ground (<20 μm) NaCl. The switching field distributions and activation volumes of two different sizes of particles are presented, 4 and 15 nm. The samples exhibit complex structural behaviour, demonstrating how difficult it is to obtain uniform nanoparticles. We find that the 4-nm particles reverse coherently whereas the 15 nm do not due to inhomogeneous crystallinity.

Index Terms—FePt nanoparticle, L1₀ phase, phase transformation.

I. INTRODUCTION

THERMAL stability of data limits the density of information that can be stored on a hard disk. Conventional magnetic recording is quickly approaching the theoretical limit, which has generated interest in novel materials such as FePt nanoparticles [1]. The advantages of such particles include a small (<10 nm) and uniform grain size, high coercivities, and the ability to self-assemble into a regular array.

In 2000, Sun *et al.* [1] introduced a method to synthesise FePt nanoparticles in the face-centered cubic (fcc) phase that has a low anisotropy. Subsequent annealing at high temperatures is required to produce the high anisotropy ($6.6 \times 10^7 \text{ erg/cm}^3$), face-centered tetragonal (fct) phase. There are many problems associated with this high-temperature anneal, such as agglomeration and sintering which prevents the subsequent formation of a regular array [2].

A simple method to obtain fct FePt nanoparticles has been developed recently by Elkins *et al.* [3]. The fcc particles were mixed with fine ground salt (NaCl) powders and annealed. The salt powders were ball milled for more than 24 h to make particle sizes smaller than 20 μm , which then act to separate the particles during the annealing process. This prevents sintering while still allowing the phase change. The salt can then be washed out of the mixture with water to leave only monodispersed fct FePt nanoparticles. Li *et al.* found the key to obtaining monodisperse fct FePt nanoparticles was the ratio of NaCl to FePt [4]. A high ratio is required for larger particles at consistent annealing conditions, but increased temperatures and times are required for smaller particles.

In this paper, we investigate the magnetic properties of the resultant fct FePt nanoparticle powders. In particular, the switching field distribution (SFD) is an important parameter in the sphere of magnetic recording because it represents a measurement of the distribution of energy barriers in a material and affects the transition width [5]. The SFD can be determined

from measurements of the irreversible susceptibility (χ_{irr}). The unnormalized differential of a dc demagnetisation remanence curve (DCD) provides the irreversible susceptibility, $\chi_{\text{irr}}(H) = dM_r/dH$ which, when normalized to unity, gives the SFD.

Measurements of the time dependence of magnetisation $dM(H)/d\ln(t)$ supplies the magnetic viscosity (S), as shown in (1). In combination with the $\chi_{\text{irr}}(H)$, the fluctuation field, $H_f(H)$, can then be found using (2)

$$S(H) = dM(H)/d\ln(t). \quad (1)$$

From the fluctuation field, the activation volume (V_{act}) can then be determined, where k is Boltzmann's constant, T is temperature, and M_s is the saturation magnetisation, taken as 1140 emu/cm³ for bulk FePt [6]. V_{act} is a measure of the volume of material that reverses during a single coherent reversal event, i.e., the minimum bit size that could be written to a disk [5]

$$H_f(H) = S(H)/\chi_{\text{irr}}(H) = kT/V_{\text{act}}(H)M_s. \quad (2)$$

II. EXPERIMENTAL PROCEDURES

Two samples of fct FePt nanoparticle powders with varying particle diameter, 4 and 15 nm, have been studied. Each sample was synthesized using the method of Sun *et al.* [1] and annealed with fine ground (<20- μm particles) NaCl at 700 °C for 4 h in forming gas (95%Ar+5%H₂) [3], [4]. The FePt powder was set in an epoxy resin for containment and the measurements were performed at 273 K on an Oxford Instruments Vibrating Sample Magnetometer with a ± 90 kOe field range.

The DCD measurements were made by saturating the sample, applying a negative field and measuring the remanent magnetisation. The sample was then resaturated, and the procedure was repeated at fields over the SFD. The time dependence measurements were made by saturating the sample, applying the required negative field and measuring the resulting decay for 600 s. This process was also repeated at fields over the whole SFD.

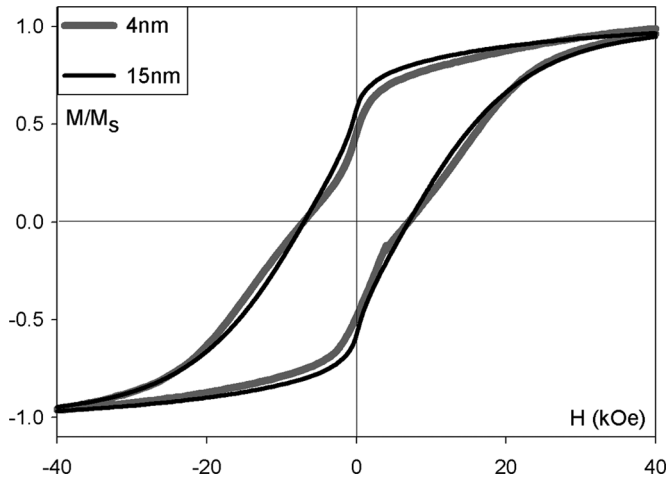


Fig. 1. Hysteresis loops for 4- and 15-nm FePt nanoparticles ($H_c = 7.3$ and 7.2 kOe respectively).

III. RESULTS AND DISCUSSION

Fig. 1 shows the hysteresis loops for the 4- and 15-nm samples, with coercivities, $H_c = 7.3$ and 7.2 kOe, respectively. From the loops, it can be seen that the reversal process is nonuniform. This is seen from the variations in gradient over the recoil branch of the hysteresis loop. There are two possible origins of this effect associated with either multimodal particle size distributions or variations in the crystallographic structure of the particles.

From previous work [3], it is believed that the salt annealing process produces a uniform particle size distribution and, hence, we conclude that this indicates that there are several phases in the particles. However, the presence of a bimodal distribution due to some small degree of sintering cannot be completely excluded. Of course, given that the energy barrier distribution which governs all magnetic measurements depends on the product KV , it is not possible to distinguish the effect of multimodal behavior in either from such measurements alone. There is evidence of a soft phase reversing at small fields in both samples. In the remainder of the loop there are several more phases that can be seen. It is clear that the variations in the loop are less pronounced for the larger particle size. This indicates that the larger particles are of uniform phase.

Given that for the smallest particle size (4 nm) the apparent multiphase behavior is more pronounced, we conclude that each particle is most likely of a uniform phase and that the variation must be occurring within different particles.

This would appear reasonable since the smallest particles consist of only about ~ 500 atoms of Fe and Pt, whereas the larger particles consist of $\sim 32\,000$ atoms. Hence, the prospect of atomic rearrangement to produce a more uniform fct structure is obviously more likely with a greater number of atoms. For the smallest sizes there also exists the possibility of chemical inhomogeneity from particle to particle.

The squareness and slope of the magnetization at coercivity also increase with particle size. This arises due to the increased particle diameter, but also the more consistent anisotropy within the 15-nm nanoparticles.

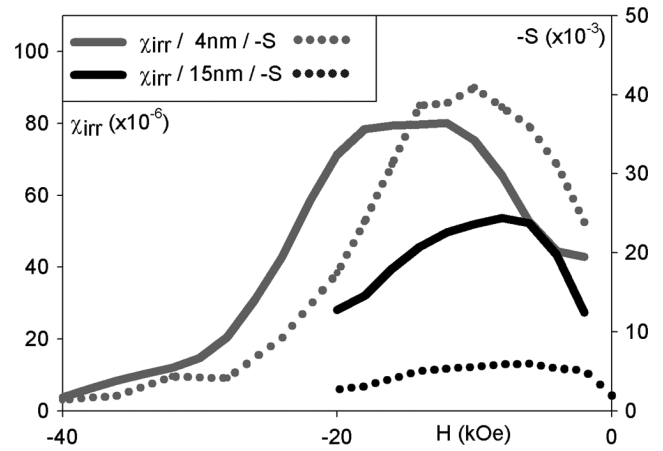


Fig. 2. Irreversible susceptibility (χ_{irr}) and magnetic viscosity (S) for 4- and 15-nm FePt nanoparticles.

Fig. 2 shows the irreversible susceptibility ($\chi_{irr}(H)$) and magnetic viscosity ($S(H)$) for the two particle sizes. The multiple phases, which are so obvious in the loops, are less obvious in χ_{irr} . The reason why these curves do not show the multiphase behavior seen in Fig. 1 is because of the spacing of the field points. The Oxford Instruments magnetometer is mounted in a superconducting solenoid which has a limited sweep-rate due to the voltage available from the power supply. This means that, within a reasonable time scale, only a limited number of field values can be selected. This is particularly true for measurements of irreversible magnetization carried out in the second and third quadrants of the loop, due to the necessity to resaturate the sample in a positive field between each measurement.

It is interesting to note that the peak in the irreversible susceptibility occurs at higher fields for the smaller particle size despite the fact that the values of H_c are very similar. The peak occurs near the coercivity (7.2 kOe) for the 15-nm particles, whereas it is much closer to twice the coercivity, ~ 14 kOe, for the 4-nm particles. This is due not only to the variation in the phases within each sample, but may also be due to the highly complex and nonuniform crystallinity of the larger particles [3].

An example of this complex crystallinity is shown in Fig. 3, where six crystallographic domains can be seen in an HRTEM image of a 15-nm particle [3]. Over 50% of the particles have been observed to contain crystallographic domains. The effect of such domains on magnetisation reversal in particles of this size is not known but the resulting dispersion in the anisotropy directions would be expected to lead to incoherent reversal. One method to examine reversal mechanisms is via studies of the activation volume determined from magnetic viscosity [7].

The magnetic viscosity for both systems was found to be linear with $\ln(t)$ as expected for a randomly oriented system, allowing the determination of S from (1). The variation of $S(H)$ is also shown in Fig. 2.

The magnitudes of the magnetic viscosity peaks are vastly different for the two sizes of nanoparticles. The magnetisation of the 4-nm nanoparticles is more susceptible to thermal fluctuations, which is to be expected for smaller volumes. However the measured coercivities for the two systems are very similar

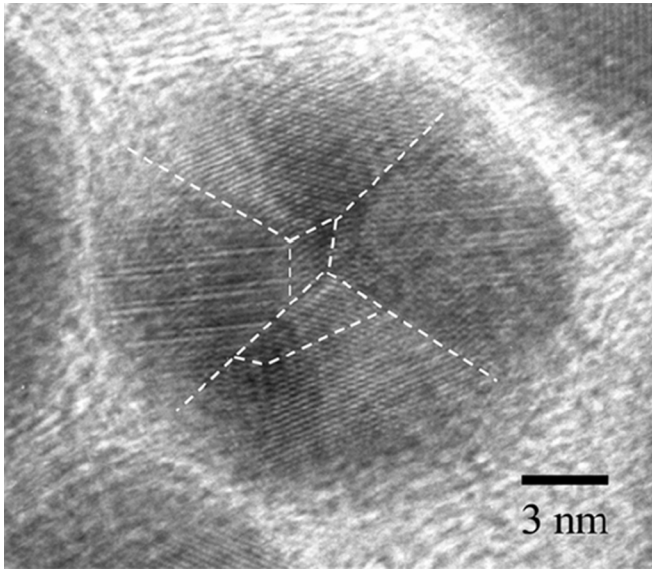


Fig. 3. HRTEM image of an annealed fct FePt nanoparticle showing the polycrystalline morphology [3].

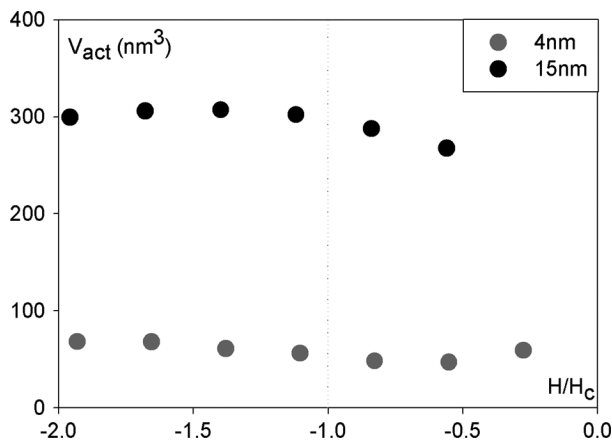


Fig. 4. Activation volumes (V_{act}) for 4- and 15-nm FePt nanoparticles.

despite the factor 4 difference in diameter (factor 64 in volume). This is due to the well-known superparamagnetic criterion for the coercivity, (3), where H_K is the anisotropy field

$$KV(1 - H_c/H_K)^2 = 25kT. \quad (3)$$

This gives a $(1 - D^{-3/2})$ dependence for the variation of coercivity with particle diameter, D . In the case of our high anisotropy FePt particles both the 4- and 15-nm particles are on the flat part of the curve, hence giving little variation in H_c .

H_f was calculated from χ_{irr} and S , from which $V_{act}(H)$ was calculated, using (2). Fig. 4 shows the variation of $V_{act}(H)$ for

both particle sizes, where a value of 1140 emu/cc has been used in (2) and [6]. For both samples there is a slight variation in V_{act} with field. Taking volumes in the region of the coercivity we would expect that the V_{act} would correlate with the average particle size. For the 4-nm particles, this is indeed the case with V_{act} corresponding to a particle diameter of 4.6 nm. However, the value of the equivalent diameter for the 15-nm system is only 8.2 nm. This is a surprising result and is indicative of incoherent reversal in these particles [7].

We believe that the origin of the incoherent reversal may be in the crystallographic domains in the 15-nm particles and the resulting anisotropy dispersion. This in turn will lead to regions within the particle having different effective switching fields and, hence, activation volumes. However, the exchange coupling within the grain will lead to single step reversal but via an incoherent mode.

In conclusion, we have shown that magnetisation reversal in highly uniform FePt nanoparticles can be complex due to incoherent modes resulting from a complex crystallographic features. Advanced magnetic measurement techniques have shown a remarkable agreement between the typical number of crystallographic domains and the activation volume of reversal.

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